

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

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Applicant: Barker et al.

Group Art Unit: 1745

Examiner: Chaney, C.

Title: LITHIUM-BASED ACTIVE
MATERIALS AND PREPARATION THEREOF

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF BIYING HUANG, Ph.D UNDER 37 C.F.R. §1.132

Dear Sir:

I, Biying Huang, hereby declare that:

- 1) I am a Research Scientist currently employed by Valence Technology, Inc ("Valence"). I have been employed by Valence since mid-2002.
- 2) I finished my undergraduate education in the department of chemistry in Nanning Normal College, of Guangxi, China. I received a Masters in Science degree in chemistry from North-Eastern Normal University of Jilin, China, with a focus in physical and material synthesis chemistry. I received a Ph.D in material chemistry from The Institute of Physics, Chinese Academy of Sciences, Beijing China, with a focus in rechargeable battery technology and electrochemistry.

- 3) From late-1996 to mid-2002, I was employed as a Postdoctoral Associate and a Research Associate with the Advanced Lithium Battery Group in the Department of Materials Science and Engineering at Massachusetts Institute of Technology ("M.I.T."). While at M.I.T, I conducted research relating to rechargeable lithium batteries, particularly new polymer electrolytes as well as new anode and cathode materials for rechargeable lithium batteries.
- 4) I am a named author of over eighty (80) scientific and conference papers relating to rechargeable lithium batteries.
- 5) I reviewed U.S. Patent No. 6,514,640 to Armand et al. (Armand '640), with particular attention to Example 2. I have also reviewed the above-identified Application, particularly the examples relating to Applicants' $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ and $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$ cathode active materials. The purpose of my review was to compare the published electrochemical performance of the modified olivine cathode material described in Example 2, against Applicants' $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ and $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$ cathode active materials described in Applicants' Application.
- 6) Because Example 2 of Armand '640 does not specify certain information concerning how the test cell was constructed (e.g. the amount of cathode active material present in the cathode or the surface area of the cathode), or how the test cell was cycled (e.g. charge and discharge rate), I was unable to convert the published electrochemical performance results in Example 2 to a unit of measurement (e.g., $\text{mA}\cdot\text{hr}/\text{gr}$) which would allow me to compare the capacities and first-cycle losses of the cathode material of Example 2, against Applicants' $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ and $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$ cathode materials. Accordingly, in accordance with the teachings of Example 2 of

Armand '640, I synthesized the modified olivine cathode material described in Example 2 so that I could construct and cycle test cells in a manner which would allow a direct comparison between modified olivine cathode material of Example 2 and Applicants' $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ and $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$ cathode materials.

- 7) In accordance with the teachings of Example 2 of Armand '640, a modified olivine cathode material was prepared as follows:
- a. A slurry was formed by mixing the following reagents with 120 mL of isopropanol:
 - i. 12.95 gr. iron oxalate ($\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$) (Aldrich);
 - ii. 8.31 gr. lithium dihydrogen phosphate (LiH_2PO_4);
 - iii. 1.52 gr. lithium oxalate ($\text{Li}_2\text{C}_2\text{O}_4$) (Alpha Organics);
 - iv. 2.94 gr. ammonium titanyl oxalate monohydrate
($(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$); and
 - v. 2.68 gr. polydiethoxysiloxane (Gelest, Inc.)
 - b. For two days, the slurry was ball-milled with sintered zirconia balls in a polyethylene container. After ball-milling, the slurry was evaporated to dryness to form a dry mixture.
 - c. The dry mixture was heated in a furnace at 350°C in an argon atmosphere (< 6 ppm oxygen) for 4 hours, and then heated at 750°C in the same atmosphere for an additional 8 hours to yield the cathode material.
 - d. Example 2 of Armand '640 does not specify the furnace oven dwell time(s). Also, the second heating temperature was not discernable from Example 2 of the Armand '640. Accordingly, based on my experience, I selected a 4 hr and

8 hr dwell time for the first and second heating temperature, respectively, and I selected 750°C to be the second heating temperature. In my opinion, a difference of $\pm 50^\circ\text{C}$ for the second heating temperature should have little or no effect on the electrochemical performance of the cathode material described in Example 2 of Armand '640.

- e. The cathode material was analyzed by X-ray diffraction spectroscopy using $\text{CuK}\alpha$ radiation, $\lambda = 1.5405$ angstroms (\AA). A copy of the results of the XRD analysis is attached as Exhibit A. The XRD spectra contained many peaks not attributable to the olivine structure, indicating that the cathode material was impure.

8) Four lithium-metal electrochemical test cells and four lithium-ion rocking-chair electrochemical test cells were constructed and tested as follows.

- a. For the cells of Set A (defined below), the positive electrode was a film containing 83.11% (by weight) of the active material, 6.76% of Super P carbon (available from 3M of Minneapolis, Minnesota) conductive carbon, and 10.13% poly(vinylidene) difluoride (PVdF), coated onto an aluminum current collector.
- b. For the cells of Set B (defined below), the positive electrode was a film containing 82.93% (by weight) of the active material, 9.76% Super P conductive carbon, and 7.31% poly(vinylidene) difluoride (PVdF), coated onto an aluminum current collector.
- c. For all cells, the electrolyte was formed by dissolving 1M LiPF_6 in a 2:1 by volume mixture of ethylene carbonate(EC)/dimethyl carbonate (DMC).

- d. For all cells, lithium metal foil and a MCMB film were employed in the anode for the lithium-metal cell and the lithium-ion cell, respectively. The MCMB film contained 88.0% (by weight) 25-28 MCMB (available from Osaka Gas of Japan), 4.0% Super P conductive carbon, and 8% PVdF binder.
 - e. For all cells, a prismatic-type cell was constructed, and a Celgard 2300 separator was interposed between the cathode and anode. The cathode had a surface area of 14.72 cm^2 , and the anode had a surface area of 18.87 cm^2 . Although differences between my cell construction and the cell construction described in Applicants' application may exist, in my experience cell construction generally has little or no effect on charge and discharge capacities.
- 9) A first set (Set A) of four cells (two lithium metal cells and two lithium-ion cells) were each cycled at 23°C , with cut-off voltage of between 2.5 V and 3.9V. Each lithium metal cell was cycled at 0.3 mA/cm^2 , and each lithium-ion cell was cycled at 0.136 mA/cm^2 .
- a. The first lithium metal cell exhibited a discharge capacity of $65.65 \text{ mA}\cdot\text{hr/gr}$ and a charge capacity of $84.53 \text{ mA}\cdot\text{hr/gr}$, with a first cycle capacity loss of 22.33%. The second lithium metal cell exhibited a discharge capacity of $46.80 \text{ mA}\cdot\text{hr/gr}$ and a charge capacity of $61.63 \text{ mA}\cdot\text{hr/gr}$, with a first cycle capacity loss of 24.00%. A voltage vs. time plot and a discharge capacity vs. cycle number plot is for both cells is attached as Exhibit B.
 - b. The first lithium-ion cell exhibited a discharge capacity of $54.99 \text{ mA}\cdot\text{hr/gr}$ and a charge capacity of $70.84 \text{ mA}\cdot\text{hr/gr}$, with a first cycle capacity loss of

22.37%. The second lithium-ion cell exhibited a discharge capacity of 54.99 mA•hr/gr and a charge capacity of 66.20 mA•hr/gr, with a first cycle capacity loss of 17.00%. A voltage vs. time plot and a discharge capacity vs. cycle number plot is for both cells is attached as Exhibit C.

10) A second set (Set B) of four cells (two lithium metal cells and two lithium-ion cells) were each cycled at 23°C, with cut-off voltage of between 2.5 V and 4.0 for lithium metal cells and 2.5 V and 3.6 V for lithium ion cells. Each lithium metal cell was cycled at 0.2 mA/cm², and each lithium-ion cell was cycled at a charge current of 0.2 mA/cm² and a discharge current of 0.136 mA/cm².

- a. The first lithium metal cell exhibited a discharge capacity of 63.33 mA•hr/gr and a charge capacity of 82.60 mA•hr/gr, with a first cycle capacity loss of 23.33%. The second lithium metal cell exhibited a discharge capacity of 63.28 mA•hr/gr and a charge capacity of 82.38 mA•hr/gr, with a first cycle capacity loss of 23.18%. A voltage vs. time plot and a discharge capacity vs. cycle number plot is for both cells is attached as Exhibit D.
- b. The first lithium-ion cell exhibited a discharge capacity of 59.48 mA•hr/gr and a charge capacity of 76.74 mA•hr/gr, with a first cycle capacity loss of 22.5%. The second lithium-ion cell exhibited a discharge capacity of 60.12 mA•hr/gr and a charge capacity of 76.22 mA•hr/gr, with a first cycle capacity loss of 21.12%. A voltage vs. time plot and a discharge capacity vs. cycle number plots for both cells is attached as Exhibit E.

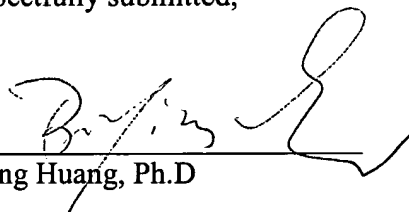
11) The electrochemical performance results I obtained for the eight electrochemical cells (Sets A and B) I constructed are summarized in Exhibit F. The electrochemical performance results for the $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ and $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$ cathode materials described in pages 45 - 48 of Applicants' Application, are also summarized in Exhibit F. Exhibit F illustrates that Applicants' $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ and $\text{LiFe}_{0.8}\text{Mg}_{0.2}\text{PO}_4$ cathode materials exhibit superior first charge and discharge capacities, and less first-cycle loss, compared to the modified olivine material I synthesized according to Example 2 of Armand '640.

12) I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Dated: October 16, 2003

By:


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